

Effects of Metal Ions and *N*-Donor Ligands with Different Coordination Characters on the Construction of d^{10} Metal-organic Complexes with Selective Photocatalytic Activities

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Four new d^{10} metal-organic coordination polymers, $[\text{Zn}(\text{L})(\text{phen})(\text{H}_2\text{O})]$ (**1**), $[\text{Cd}(\text{L})(\text{phen})]$ (**2**), $[\text{Zn}(\text{L})(\text{bppdc})]\cdot 3\text{H}_2\text{O}$ (**3**), and $[\text{Cd}(\text{L})(\text{bppdc})]\cdot 3\text{H}_2\text{O}$ (**4**) [$\text{L} = 2$ -carboxymethylsulfanyl nicotinic acid, phen = 1,10-phenanthroline, bppdc = *N,N'*-bis(pyridin-3-yl)pyridine-2,6-dicarboxamide], have been obtained from hydrothermal reactions of zinc(II)/cadmium(II) nitrates with the semi-rigid *N/S*-containing dicarboxylate L, and the two structurally disparate neutral *N*-donor ligands phen and bppdc. Single-crystal X-ray diffraction analysis has revealed that compound **1** is a one-dimensional (1-D) helical coordination polymer linked by Zn^{II} atoms and L spacers. Compound **2** features a double-chain structure connected *via* binuclear Cd^{II} units and pairs of L linkers. Adjacent chains of **1** and **2** are packed into 3-D supramolecular networks by hydrogen bonds and π - π stacking interactions. Compounds **3** and **4** exhibit similar 2-D (4,4)-connected wave-like networks based on linear $[\text{M-L}]_n$ and zigzag $[\text{M-bppdc}]_n$ metal-organic chains ($\text{M} = \text{Zn}^{\text{II}}$ for **3** and Cd^{II} for **4**). The effects of metal ions and *N*-donor ligands with different coordination characters are discussed. Moreover, the photoluminescence properties and photocatalytic activities of compounds **1–4** were investigated.

Key words: Hydrothermal Syntheses, Crystal Structures, d^{10} Metal-organic Coordination Polymers, Photoluminescence, Photocatalytic Activities

Introduction

The construction of d^{10} metal-organic coordination polymers has attracted considerable attention in recent years not only due to their structural diversity but also owing to the extensive potential applications in gas storage, ion sensors, luminescent probes and others [1–5]. One of the powerful approaches to generate such organic-inorganic functional materials with low solubility is the rational selection of central metal ions and organic ligands for complexation under hydrothermal conditions [6–8]. Owing to the variations of steric effects, coordination priority and orientation of the organic ligands, as well as the tunable coordination number, radius and charge of the metal ions, the mechanism of the influence of these parameters on the structures of the target compounds is still unpredictable [9–12]. Thus, it continues to be meaningful to investigate the effects of the metal ions and organic ligands on tailoring the architectures of coordination compounds.

Recently, *S*-containing organic dicarboxylates with *N*-heterocyclic ring spacers have attracted more interest in combination with multidentate *N*-donor ligands (*e.g.* chelating dipyrindino-[3,2-*d*:2',3'-*f*]quinoxaline (dpq), and bridging 1,3-bis(4-pyridyl)propane (bpp) or 4,4'-bipyridine (4,4'-bipy)) in constructing the target coordination compounds [13–15]. However, the effects of the *N*-donor ligands (from chelating ligands to bridging ligands) and d^{10} metal ions on coordination compounds derived from *S/N*-containing dicarboxylates have received less attention [16].

Based on the above viewpoints and as a continuation of our research on the dicarboxylate-based coordination compounds [17–21], in this work, we selected semi-rigid 2-carboxymethylsulfanyl nicotinic acid (H_2L) as the main ligand, and two structurally disparate neutral *N*-donors (chelating 1,10-phenanthroline (phen) and bridging *N,N'*-bis(pyridin-3-yl)pyridine-2,6-dicarboxamide (bppdc)) as the secondary ligands to react with zinc(II)/cadmium(II)

salts. The selection of phen, bppdc and H_2L is based on the following considerations: (a) phen with its aromatic ring system may provide supramolecular recognition sites for π - π aromatic stacking interactions to form supramolecular structures [5, 22]; (b) bppdc not only has two potential bridging nitrogen sites in the terminal pyridyl groups, but also possesses two potential hydrogen bonding sites for -NH and -C=O groups, which may expand bonding in the coordination and supramolecular frameworks [23–31]; (c) compared to common phthalic acid, H_2L possesses a nitrogen atom in the aromatic spacer offering supramolecular recognition abilities for hydrogen bonding interactions, which may lead to diverse supramolecular networks. Moreover, H_2L has a flexible -SCH₂- group, favoring strain-free coordination frameworks [16].

Four new Zn^{II}/Cd^{II} compounds, [Zn(L)(phen)(H₂O)] (**1**), [Cd(L)(phen)] (**2**), [Zn(L)(bppdc)]·3H₂O (**3**), and [Cd(L)(bppdc)]·3H₂O (**4**), have been obtained from the hydrothermal reactions. The effects of the metal ions and the *N*-donor ligands on the architectures of the title compounds are discussed. Moreover, the photoluminescent properties and photocatalytic activities of compounds **1–4** were investigated.

Results and Discussion

Crystal and molecular structure of [Zn(L)(phen)(H₂O)] (**1**)

The determination of the structure by single-crystal X-ray diffraction has revealed that compound **1** is

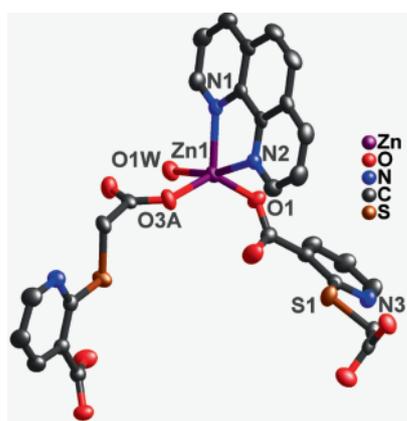


Fig. 1 (color online). The coordination environment of the Zn^{II} ion in compound **1**.

a 3-D supramolecular framework derived from 1-D helical coordination polymers extended by hydrogen bonds and π - π stacking interactions. Each Zn^{II} atom in **1** is penta-coordinated by two nitrogen atoms from one phen ligand, two oxygen atoms from two carboxylate groups of different L anions and one water molecule in a distorted trigonal bipyramidal geometry (Fig. 1). The bond lengths around Zn^{II} atoms range from 1.9938(17) to 2.1619(19) Å for Zn–O, and are 2.1293(19) and 2.166(2) Å for Zn–N, which are all within the normal range of distances of analogous compounds [9–12]. The O–Zn–N angles are between 88.43(7) and 165.96(7)°. The N–Zn–N angle is 77.54(7)°, and the O–Zn–O angles are in the range 8.70(7)–132.63(7)°. The Zn^{II} coordination polyhe-

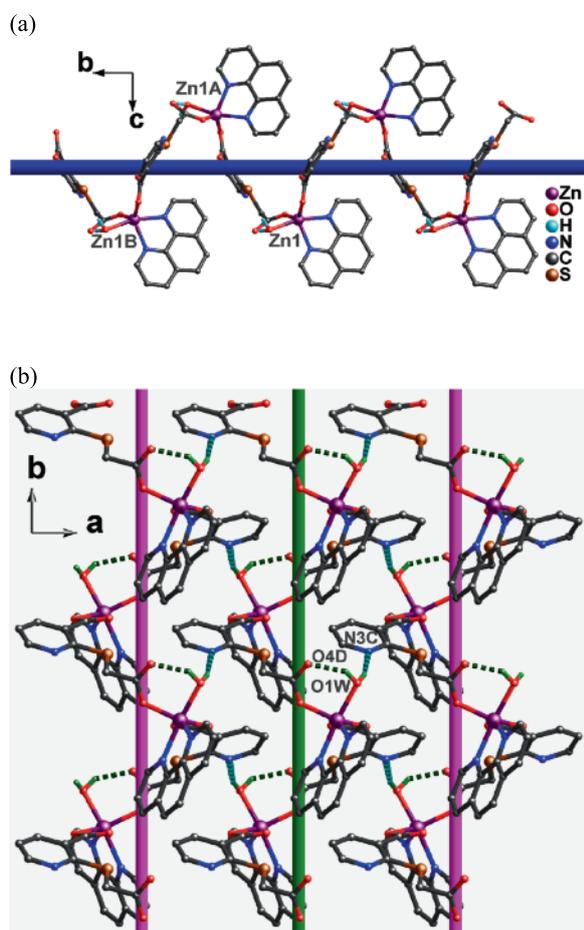


Fig. 2 (color online). (a) A helical chain linked by L anions and Zn^{II} ions in **1**; (b) 2-D supramolecular network in **1** derived from helical chains bridged by hydrogen bonding interactions.

dron is slightly distorted caused by the steric effect of the different N/O -donor ligands (Table S1; Supporting Information available online. See note at the end of the paper for availability).

In complex **1**, the phen ligand adopts the familiar chelating coordination mode. Each L anion links the metal-organic units in a bis-monodentate coordination mode to generate a chain (Fig. 2a). Owing to the twist of the L anions, the chain exhibits a helical feature with a pitch of 9.17 Å. Furthermore, adjacent chains are linked *via* hydrogen bonding interactions between the oxygen atoms from coordinated water molecules and the uncoordinated nitrogen atoms of the pyridyl groups of L anions to generate a 2-D supramolecular network parallel to the *ab* plane ($O1W-H1WB\cdots N3(C) = 2.05(3)$ Å, $163(3)^\circ$; C: $2-x, 1/2+y, 1/2-z$) (Fig. 2b). Moreover, intramolecular hydrogen bonding interactions between coordinated water molecules and carboxylic oxygen atoms stabilize the 2-D structure ($O1W-H1WA\cdots O4(D) = 1.93$ Å, 146° ; D: $1-x, 1/2+y, 1/2-z$). Finally, the supramolecular layers are linked by π - π stacking interactions between the aromatic rings of phen to generate a 3-D supramolecular architecture (Fig. S1; Supporting Information). The distance between ring centroids ($Cg\cdots Cg$) of pyridyl ($Cg1 = N1-C1-C2-C3-C4-C12$) and phenyl rings ($Cg2 = C4-C5-C6-C7-C11-C12$) is 3.573(3) Å, and the corresponding dihedral angle is 0.58° . $Cg1\cdots Cg2$ is 3.533(3) Å, and the dihedral angle is 0° .

Crystal and molecular structure of $[Cd(L)(phen)]$ (**2**)

To study the effect of the metal ion on the structure of the coordination compound, the cadmium(II) analog of **1** has been prepared. A 3-D supramolecular architecture of **2** constructed from double-chains connected by π - π and C-H \cdots π stacking interactions was obtained. As shown in Fig. 3, each Cd^{II} atom is seven-coordinated by five oxygen atoms from three carboxylic groups of three different L anions and two chelating nitrogen atoms from a phen ligand. The Cd-O distances are in the range 2.2415(16)–2.644(2) Å, and the Cd-N distances are 2.3644(18) and 2.3671(18) Å, which are near the normal range [9–12]. The O–Cd–N angles are in the range $79.83(6)$ – $149.35(6)^\circ$. The O–Cd–O angles range from $52.43(6)$ to $131.06(6)^\circ$, and the N–Cd–N angle is $70.43(6)^\circ$ (Table S2; Supporting Information).

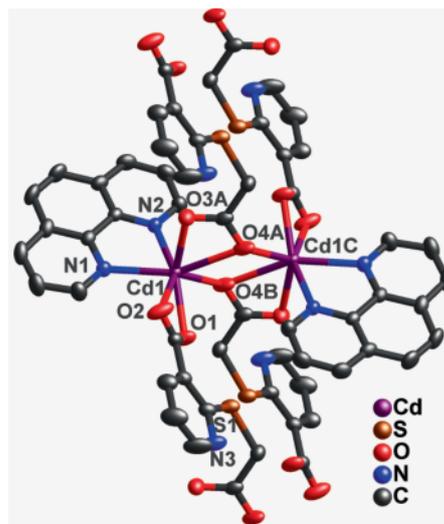


Fig. 3 (color online). The coordination environment of the Cd^{II} ion in compound **2**.

It is notable that the two carboxylic groups of the L anion in compound **2** exhibit unsymmetrical chelating-bridging coordination modes. The two μ_2 -O atoms (O4A and O4B) from two carboxylate groups (μ_2 - η^2 : η^1) connect two adjacent Cd^{II} atoms to generate a bimetallic subunit with a $Cd1\cdots Cd1C$ distance of 3.965 Å. The subunits are connected *via* pairs of L anions to form a double-chain coordination polymer (Fig. 4), and the distance between the cores of the subunits is 9.155 Å. Furthermore, the adjacent chains are linked by intermolecular π - π stacking interactions between the pyridyl ($Cg3 = N1-C11-C10-C9-C8-C12$) and phenyl ($Cg4 = C1-C5-C6-C7-C8-C12$) rings to generate a layer parallel to the *ac* plane

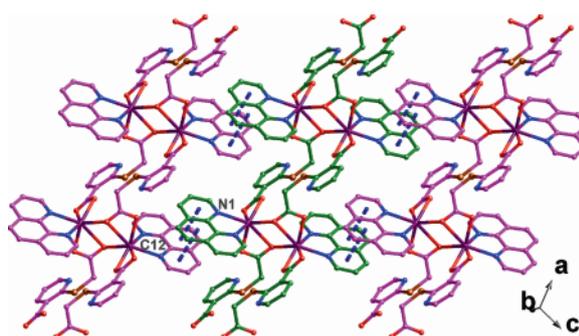


Fig. 4 (color online). 2-D Supramolecular network of **2** based on 1-D double chains linked by π - π stacking interactions.

(Fig. 4). $Cg3 \cdots Cg4$ is $3.6725(15)$ Å, and the corresponding dihedral angle is 3.14° . Finally, the adjacent parallel layers are bridged by $C-H \cdots \pi$ interactions between the phenyl ring of phen ($Cg4$) and the pyridyl ring (containing $C15$) forming a 3-D supramolecular architecture ($C15-H15A \cdots Cg5(D) = 2.78$ Å, 126° ; D: $x, -1 + y, z$) (Fig. S2; Supporting Information).

Crystal and molecular structure of $[Zn(L)(bppdc)] \cdot 3H_2O$ (3) and $[Cd(L)(bppdc)] \cdot 3H_2O$ (4)

To evaluate the effect of the neutral N -donor ligands on the structure of the coordination compounds, we selected a bridging V-type tri-pyridyl-bis-amide ligand to react with zinc(II)/cadmium(II) salts and H_2L . Complexes **3** and **4** are isostructural in the solid state, crystallizing in space group Cc with $Z = 4$. As shown in Fig. 5 and Fig. S3 (Supporting Information), despite the isostructural relation there is an interesting difference in the coordination of the metal centers. The coordination number of the metal center is five at Zn^{II} in **3** and six at Cd^{II} in **4**. Tables S3 and S4 (Supporting Information) contain important bond lengths and angles for both structures. Complexes **3** and **4** form wave-like layer structures in the solid state.

In the following complex **3** is described in more detail as a representative structure. In **3**, three carboxylic oxygen atoms from two different L anions and one pyridyl nitrogen atom of the $bppdc$ ligand lie roughly in a square plane. One nitrogen atom of another pyridyl group from $bppdc$ occupies the axial position. The $Zn-O$ distances are between $1.958(3)$ and $2.290(3)$ Å, whereas the $Zn-N$ distances are $2.080(2)$

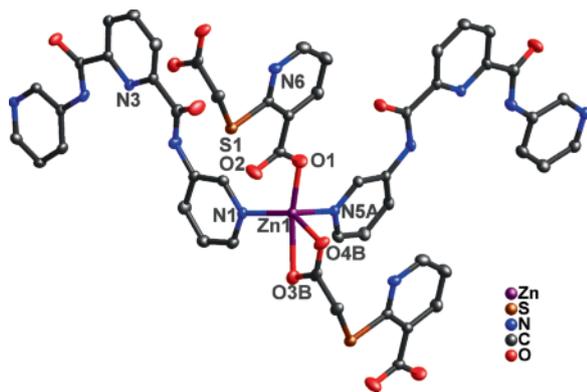


Fig. 5 (color online). The coordination environment of the Zn^{II} ion in compound **3**.

and $2.083(2)$ Å. The $O-Zn-N$ angles are between $90.19(9)$ and $106.53(11)^\circ$. The $N-Zn-N$ angle is $103.70(9)^\circ$, and the $O-Zn-O$ angles are in the range $59.04(9) - 160.40(10)^\circ$. Owing to the steric effect of the different N/O donor ligands, the Zn^{II} coordination polyhedron is slightly distorted (Table S3; Supporting Information).

In compound **3**, $bppdc$ acts as bridging ligand to link the Zn^{II} atoms forming a $[Zn-bppdc]_n$ zigzag

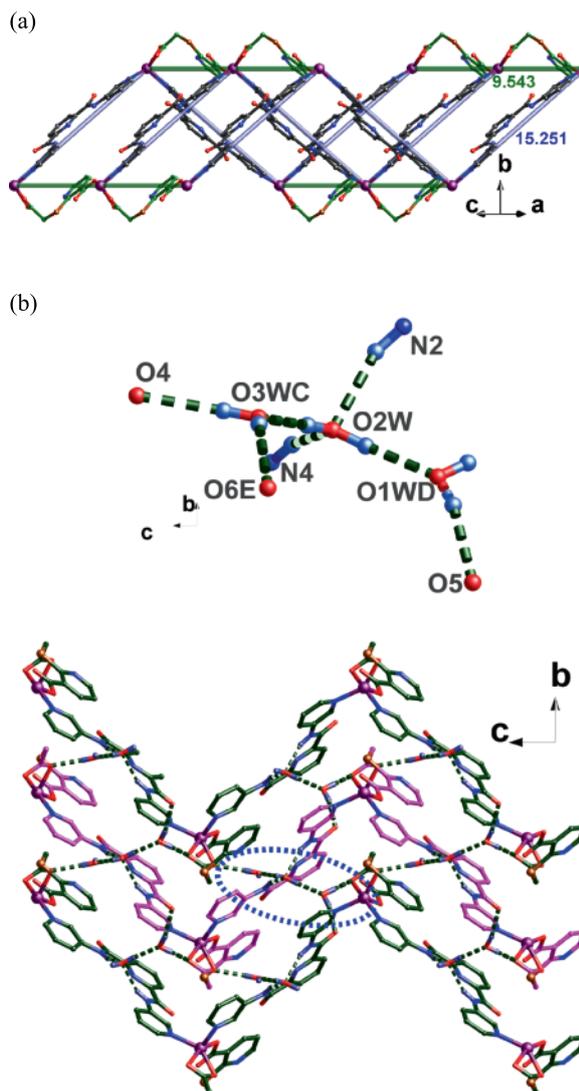


Fig. 6 (color online). (a) View of the wave-like layer linked by L and $bppdc$ of **3**; (b) 3-D supramolecular framework (bottom) derived from layers bridged by trinuclear cluster (top), for compound **3**.

chain along the c axis (Fig. 6a). The Zn...Zn distance is 15.251 Å. The nitrogen atoms N1 and N5 of the terminal pyridyl groups from the bppdc ligand turn to the outside orientation with an N...N distance of 11.338 Å, and the corresponding dihedral angles between the terminal and middle pyridyl rings are 4.14 and 6.78°, which is different from that in related compounds [30]. Furthermore, the adjacent chains are connected by L anions with chelating-monodentate coordination mode to generate a wave-like 2-D (4,4)-connected network (Fig. 6a). The Zn...Zn distance bridged by the L anion is 9.543 Å. It is notable that three water molecules are linked by hydrogen bonding interactions to form a trinuclear water cluster (O2W–H2WA...O3W(C) = 2.766(5) Å, 176 (4)°; C: $1+x$, $1-y$, $1/2+z$; O2W–H2WB...O1W(D) = 2.803(5) Å, 171 (5)°; D: $1/2+x$, $-1/2+y$, z ; O3W–H3WB...O6(E) = 3.096(5) Å, 152 (6)°; E: x , $1-y$, $-1/2+z$) (Fig. 6b top). The trinuclear water cluster stabilizes the 2-D coordination network *via* hydrogen bonding interactions including -NH groups from bppdc (N2–H2A...O2W = 3.082(4) Å, 150°; N4–H4B...O2W = 3.017(4) Å, 156°). Finally, the trinuclear water cluster links the adjacent 2-D coordination networks to generate a 3-D supramolecular architecture through hydrogen bonding interactions with carboxylic oxygen atoms of L anions (O1W–H1WA...O5 = 2.957(5) Å, 166 (5)°; O3W–H3WA...O4 = 2.835(5) Å, 172 (6)°) (Fig. 6b, bottom).

Effects of metal ions and N -donor ligands on the architectures

From the description above, the d^{10} metal ions with different radii as well as N -donor ligands containing disparate coordination character show a significant influence on the resulting structures of the title compounds (Fig. S4). In compounds **1** and **2**, the same dicarboxylate ligand L and the N -donor ligand phen were used to react with Zn^{II} and Cd^{II} ions. However, the Zn^{II} ion in **1** shows a penta-coordinated mode with trigonal bipyramidal geometry. The L anion exhibits $\mu_1-\eta^0:\eta^1/\mu_1-\eta^0:\eta^1$ coordination mode, which links the Zn^{II} ions to form a helical chain, while in **2**, the Cd^{II} ion features seven-coordination, and the L anion exhibits $\mu_1-\eta^1:\eta^1/\mu_2-\eta^1:\eta^2$ coordination mode and connects the Cd^{II} ions to generate a double-chain. On the other hand, in compounds **3** and **4**, the same dicarboxylate L and N -donor ligands bppdc were se-

lected to combine with Zn^{II} and Cd^{II} ions. The Zn^{II} ion in **3** shows a penta-coordinated mode with tetragonal-pyramidal geometry. The L anion exhibits $\mu_1-\eta^1:\eta^1/\mu_1-\eta^0:\eta^1$ coordination mode and bridges the Zn-bppdc zigzag chains to form a 2-D wave-like network. A similar 2-D network was obtained in **4**, however, the Cd^{II} ion in **4** is in six-coordinated mode, and the L anion exhibits $\mu_1-\eta^1:\eta^1/\mu_1-\eta^1:\eta^1$ coordination mode, clearly different from **3**. The results indicate that similar d^{10} metal ions with different radii may lead to diverse coordination architectures. In addition, compared to the phen-based compounds **1–2**, the bppdc-based compounds **3–4** feature higher-dimensional structures due to the bridging coordination character of the bppdc ligand.

PXRD measurements of the title compounds

Powder X-ray diffraction (PXRD) experiments were carried out for compounds **1–4** in order to confirm the phase purity of the bulk materials (Fig. S5; Supporting Information). The as-synthesized patterns are in good agreement with the corresponding simulated ones, which indicates the phase purity of the samples.

Photoluminescence properties of compounds **1–4**

Metal-organic compounds based on Zn^{II}/Cd^{II} ions have been shown to exhibit interesting photoluminescence properties [4, 12]. In the present work, to study the fluorescence properties of the title compounds, the emission spectra of compounds **1–4** in the solid state at ambient temperature were measured. As shown in

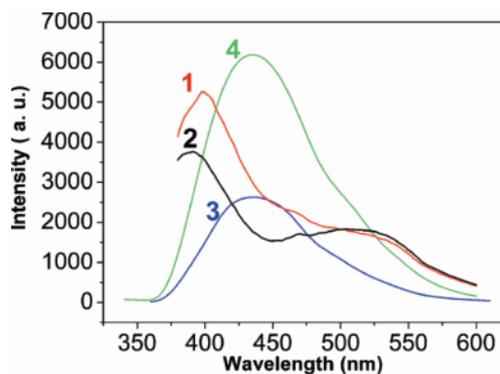


Fig. 7 (color online). Fluorescence spectra of **1–4** in the solid state at room temperature.

Fig. 7, compounds **1** and **2** show blue photoluminescence with the emission maximum at *ca.* 398 and 391 nm upon excitation at 315 and 320 nm. Compared with the maximum emission of the free ligand phen ($\lambda_{\text{ex}} = 310$ nm, $\lambda_{\text{em}} = 388$ nm) [32], a red shift of *ca.* 10 nm (for **1**) and *ca.* 3 nm (for **2**) have been observed. The blue/green emission bands of **3** and **4** are at about 434 and 436 nm ($\lambda_{\text{ex}} = 295$ nm for **3**, and $\lambda_{\text{ex}} = 305$ nm for **4**). Compared with the free ligand bppdc ($\lambda_{\text{ex}} = 280$ nm, $\lambda_{\text{em}} = 431$ nm) [30], the emissions of the title compounds exhibit a red shift of *ca.* 3 nm for **3** and *ca.* 5 nm for **4**. It is well known that the carboxylate ligands show almost no contribution to the fluorescent emission, due to the weak emission resulting from a $\pi^* \rightarrow n$ transition [32]. Thus, the emissions of compounds **1–4** may be attributed to intraligand $\pi^* \rightarrow \pi$ charge transitions of phen and bppdc ligands. The rather small red shifts are probably caused

by the coordination of phen and bppdc to the metal centers [33], and reflect the limited influence of the coordination [34].

Selective photocatalytic activities of compounds **1–4**

Metal-organic compounds based on d^{10} ions exhibit attractive catalytic abilities for photodegradation of organic pollutants [29]. Methylene blue (MB), methyl orange (MO) and rhodamine B (RhB) are common pollutants from industrial sources, and their photodegradation using catalysts is a promising method [35–38]. Herein, the photocatalytic performance of compounds **1–4** on the photodegradation of MB was investigated under UV irradiation through a typical process: compound **2** (**1**, **3** and **4**, 150 mg) was dispersed in MB solution ($1 \text{ mol} \cdot \text{L}^{-1}$, 100 mL), and the suspension was magnetically stirred for about 20 min in the dark. Then

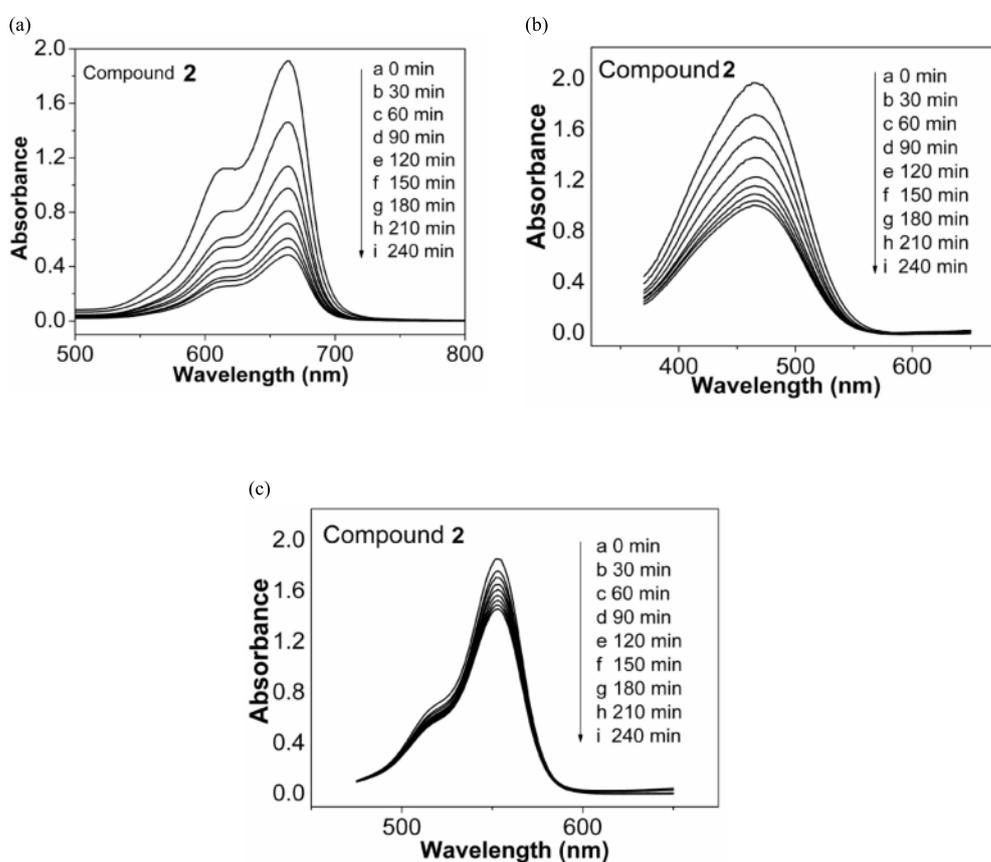


Fig. 8 (color online). Absorption spectra of the MB (a), MO (b) and RhB (c) solution during the decomposition reaction under UV light irradiation with the use of compound **2**.

the mixture was exposed to UV irradiation from a high-pressure mercury vapor lamp under continuous stirring. The suspension (5 mL) was taken for centrifugal separation every 30 min, and the transparent solution was taken out for analysis. It is well known that there is no obvious change in similar experiments without any catalyst [38]. However, it can be seen from Fig. 8a and Fig. S6 (Supporting Information) that the absorbance peaks of MB are decreased from 1.91 to 0.65 for **1**, 0.48 for **2**, 0.71 for **3**, and 0.59 for **4** after 240 min. The absorption peak of MB decreased by approximately 66% for **1**, 75% for **2**, 63% for **3**, and 69% for **4**, suggesting a catalyzing effect of the title compounds. The photocatalytic performance of the cadmium(II) compounds is much better than that of the corresponding zinc(II) compounds [29].

In order to investigate the relative photocatalytic activities of the title compounds, compound **2** was selected as a representative, and similar procedures were performed for degradation of MO and RhB. As shown in Fig. 8b, c, the absorption peak of MO decreased by approximately 49%, while the degradation of RhB is approximately 22%. Compared to the degradations of MO and RhB, compound **2** shows high photocatalytic efficiencies for the degradation of MB. Similar results were reported in our previous work [38]. However, the detailed reason is difficult to explain at the current stage.

To investigate the stability of the title compounds as photocatalysts, we repeated the PXRD experiment with the compounds after the photocatalytic experiment, and the PXRD patterns were almost identical to those of the original compounds (Fig. S5; Supporting Information). The results show that the catalysts may be recycled after the catalytic experiments.

Conclusions

In summary, four new d^{10} coordination compounds have been obtained from a semi-rigid *N*-/*S*-functional dicarboxylate L and two structurally disparate neutral *N*-donor ligands, phen and bppdc. Owing to the different coordination characters of the metal ions and *N*-donor ligands, the L anions exhibit four different coordination modes, leading to a 1-D helical chain in **1**, a double-chain in **2**, and a wave-like network in **3–4**. The results indicate that the metal ions and *N*-donor ligands play important roles in the rational design and synthesis of the structures of the target compounds.

Moreover, the compounds are candidates for photocatalytic materials.

Experimental Section

Materials and methods

H₂L was synthesized by the method described in the literature [39]. All other chemicals purchased were of reagent grade and used without further purification. FT-IR spectra (KBr pellets) were taken on a Varian 640 FT-IR spectrometer in the 500–4000 cm⁻¹ region. Powder XRD investigations were carried out with a Ultima IV with D/teX Ultra diffractometer at 40 kV, 40 mA with CuK α ($\lambda = 1.5406 \text{ \AA}$) radiation. Fluorescence spectra were recorded at room temperature on a Hitachi F-4500 fluorescence/phosphorescence spectrophotometer. UV/Vis absorption spectra were obtained using a SP-1900 UV/Vis spectrophotometer.

Synthesis of [Zn(L)(phen)(H₂O)] (**1**)

A mixture of Zn(NO₃)₂·6H₂O (0.1 mmol), H₂L (0.1 mmol), phen (0.1 mmol), H₂O (12 mL) and NaOH (0.2 mmol) was stirred for 30 min in air, then transferred and sealed in a 25 mL Teflon reactor, which was heated at 110 °C for 96 h leading to the formation of colorless block-shaped crystals of **1** (~ 26% yield based on Zn). – Elemental analysis (%) for C₂₀H₁₅N₃O₅SZn: calcd. C 50.59, H 3.18, N 8.85; found C 50.62, H 3.22, N 8.82. – IR (KBr, cm⁻¹): $\nu = 3381(\text{m}), 3270(\text{m}), 3074(\text{w}), 1620(\text{s}), 1558(\text{s}), 1517(\text{m}), 1427(\text{s}), 1390(\text{s}), 1375(\text{s}), 1355(\text{s}), 1240(\text{w}), 1162(\text{w}), 1122(\text{w}), 1080(\text{m}), 850(\text{s}), 786(\text{s}), 725(\text{s}), 634(\text{m}), 576(\text{m})$.

Synthesis of [Cd(L)(phen)] (**2**)

Similar procedures were performed to obtain colorless block-shaped crystals of compound **2**, except that Cd(NO₃)₂·6H₂O (0.1 mmol) was used instead of Zn(NO₃)₂·6H₂O (~ 30% yield based on Cd). – Elemental analysis (%) for C₂₀H₁₃N₃O₄SCd: calcd. C 47.68, H 2.60, N 8.34; found C 47.62, H 2.63, N 8.32. – IR (KBr, cm⁻¹): $\nu = 3049(\text{m}), 2923(\text{m}), 1589(\text{s}), 1515(\text{m}), 1427(\text{s}), 1380(\text{s}), 1348(\text{s}), 1336(\text{s}), 1224(\text{w}), 1143(\text{w}), 1103(\text{w}), 1074(\text{m}), 914(\text{w}), 858(\text{s}), 783(\text{s}), 727(\text{m}), 638(\text{m})$.

Synthesis of [Zn(L)(bppdc)]·3H₂O (**3**)

Compound **3** was synthesized in a similar way to that described for **1**, except that phen was replaced by bppdc. Colorless block-shaped crystals of **3** were obtained (~ 20% yield based on Zn). – Elemental analysis (%) for C₂₅H₂₄N₆O₉SZn: calcd. C 46.20, H 3.72, N 12.93; found C 46.22, H 3.7, N 12.90. – IR (KBr, cm⁻¹): $\nu = 3531(\text{m}), 3409(\text{m}), 3246(\text{m}), 2924(\text{w}), 1670(\text{m}), 1623(\text{s}), 1568(\text{s}), 1486(\text{m}), 1434(\text{m}), 1402(\text{m}), 1363(\text{s}), 1272(\text{m}), 1225(\text{m})$.

Table 1. Crystal data and structure refinement for compounds **1–4**.

	1	2	3	4
Empirical formula	C ₂₀ H ₁₅ N ₃ O ₅ SZn	C ₂₀ H ₁₃ N ₃ O ₄ SCd	C ₂₅ H ₂₄ N ₆ O ₉ SZn	C ₂₅ H ₂₄ N ₆ O ₉ SCd
Fw	474.81	503.79	649.93	696.96
Crystal system	monoclinic	triclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P\bar{1}$	Cc	Cc
<i>a</i> , Å	7.736(5)	9.1553(5)	9.5432(7)	9.6032(7)
<i>b</i> , Å	10.654(5)	9.3047(5)	13.6601(10)	13.8227(7)
<i>c</i> , Å	23.558(5)	11.9765(7)	20.9105(15)	20.8152(14)
α , deg	90	95.3840(10)	90	90
β , deg	98.162(5)	111.2200(10)	92.7650(10)	93.9550(10)
γ , deg	90	104.6500(10)	90	90
<i>V</i> , Å ³	1922.0(16)	900.50(9)	2722.7(3)	2756.5(3)
<i>Z</i>	4	2	4	4
<i>D</i> _{calcd.} , g cm ⁻³	1.64	1.86	1.59	1.68
μ (MoK α), mm ⁻¹	1.4	1.4	1.0	0.9
<i>F</i> (000), e	968	500	1336	1408
Refl. collected	10657	4785	6849	6915
Refl. unique/ <i>R</i> _{int}	3771/0.0211	3156/0.0094	3698/0.0263	4174/0.0162
Ref. parameters	275	262	403	380
<i>R</i> 1 ^a [<i>I</i> > 2 σ (<i>I</i>)]	0.0302	0.0185	0.0267	0.0231
<i>wR</i> 2 ^b (all data)	0.0736	0.0480	0.0554	0.0566
GoF ^c	1.016	1.087	0.981	1.041
<i>x</i> (Flack)	–	–	0.018(8)	–0.014(17)
$\Delta\rho_{\max/\min}$, e · Å ⁻³	0.30/–0.32	0.39/–0.46	0.23/–0.21	0.52/–0.39

^a $R1(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; ^b $wR2(F^2) = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$; ^c $GoF = [\Sigma w(F_o^2 - F_c^2)^2/(n_{\text{obs}} - n_{\text{param}})]^{1/2}$; $w = [\sigma^2(F_o^2) + (aP)^2 + bP]^{-1}$, where $P = (\text{Max}(F_o^2, 0) + 2F_c^2)/3$.

1194(w), 1128(w), 1073(m), 1029(m), 1000(w), 950(m), 894(m), 844(m), 812(m), 771(s), 749(s), 699(m), 649(m).

[Cd(L)(bppdc)]·3H₂O (**4**)

Compound **4** was synthesized in a similar way to that described for **2**, except that phen was replaced by bppdc. Colorless block-shaped crystals of **4** were obtained (~ 18% yield based on Cd). – Elemental analysis (%) for C₂₅H₂₄N₆O₉SCd: calcd. C 43.08, H 3.47, N 12.06; found C 43.02, H 3.43, N 12.02. – IR (KBr, cm⁻¹): $\nu = 3504(\text{m}), 3401(\text{m}), 3243(\text{m}), 3122(\text{m}), 2923(\text{m}), 2852(\text{m}), 1670(\text{s}), 1583(\text{s}), 1548(\text{m}), 1432(\text{m}), 1390(\text{s}), 1338(\text{m}), 1272(\text{m}), 1228(\text{m}), 1130(\text{w}), 1076(\text{m}), 998(\text{m}), 946(\text{m}), 863(\text{m}), 821(\text{m}), 809(\text{s}), 750(\text{s}), 688(\text{s}), 619(\text{m})$.

X-Ray crystallography

Crystallographic data for the title compounds were collected on a Bruker Smart APEX II diffractometer with MoK α radiation ($\lambda = 0.71069$ Å) in the range of $2.1^\circ \leq \theta \leq 26.0^\circ$ for **1**, $1.86^\circ \leq \theta \leq 25.0^\circ$ for **2**, $1.95^\circ \leq \theta \leq 25.0^\circ$ for **3**, and $1.96^\circ \leq \theta \leq 24.99^\circ$ for **4** by using an ω -2 θ scan mode. The measurement temperatures were 293(2) K for **1–4**. The structures were solved by the Direct Methods and refined by the full-matrix least-squares on F^2 using the programs SHELXS/L-97 [40–43]. All non-hydrogen atoms

were refined anisotropically. The hydrogen atoms of the water molecules of compounds **1**, **3** and **4** were located, and all other hydrogen atoms of the ligands were included in calculated positions. The crystal data and structure refinement details for compounds **1–4** are given in Table 1. Selected bond lengths and angles are given in Tables S1–S4 (Supporting Information).

CCDC 987972 (**1**), 973200 (**2**), 987966 (**3**), and 987968 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting information

Additional crystal structure plots, schematic views of the effects of *N*-donor ligands and metal ions on the coordination polymers of **1–4**, PXRD patterns of **1–4**, the absorption spectra of the MB solution during the decomposition reaction with the use of compounds **1**, **3** and **4**, and tables of bond lengths and angles in the crystal structures of **1–4** are given as Supporting Information available online (DOI: 10.5560/ZNB.2014-3326).

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